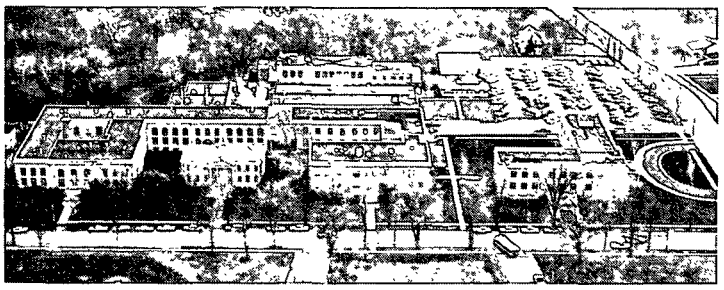

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CHARACTERIZATION OF BLACK LIQUOR DROP DRYING IN AIR

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ABSTRACT

Forced convective air drying of kraft black liquor drops was studied at temperatures below 200 C to avoid mass loss by pyrolysis. When dried in hot air, black liquor drops form a surface skin and undergo repeated cycles of inflation and rupture. Of particular interest were the influence of surface swelling and rupture on drying rate and drop temperature. Calculations which account for convection, conduction and radiation heat transfer to the drop indicate that increased drying rates should result from inflation. However, experimental drying rates were insensitive to inflation. One explanation is that nucleation of vapor bubbles in the moist drop increases resistance to conduction heat transfer. The subsequent rise in surface temperature reduces the driving force for heat transfer to the drop. The effect of increased surface area is offset by the reduction in temperature driving force. Scanning electron micrographs of dried drops showed multiple voids in the drop shell.

SCOPE

In kraft chemical recovery operations, wet black liquor drops are burned in a hot furnace. Evaporation of moisture is the first step in black liquor combustion. Previous studies of black liquor combustion have focused on subsequent stages, namely pyrolysis (volatiles burning) and char burning. Despite its potential influence on these events, very little information about black liquor drop drying exists in the literature. The purpose of this work is to study black liquor drop drying in air below the pyrolysis temperature. Low temperatures relative to the recovery furnace were chosen so that mass loss was due to drying, not pyrolysis. Certain black liquor physical properties important to drying, such as viscosity, are sensitive to solids content. The influence of initial liquor solids content on drop drying was therefore of interest.

CONCLUSIONS AND SIGNIFICANCE

Black liquor drops dried in air above the boiling point undergo cycles of inflation and rupture. However, an anticipated increase in drying rate due to droplet inflation did not occur. In addition to a large, central void, it appears that small vapor bubbles nucleate in the moist droplet shell, creating an internal heat transfer resistance analogous to a porous insulator. The increased resistance causes the surface temperature to rise. As a

result, the external driving force for heat transfer to the drop decreases and drying rate remains relatively constant. Scanning electron microscopy confirmed the existence of multiple internal voids.

Extension of these results to high temperatures suggests that significant temperature gradients may exist in black liquor drops as they dry in a recovery boiler. If inflation and rupture do not mix the drop's contents sufficiently, rapid surface heating will result in simultaneous drying and pyrolysis.

Drop drying is important to a variety of chemical process industries. Most drying operations are designed to create a dehydrated product for packaging and sale. In kraft pulp mills, however, drop evaporation is the first stage of black liquor combustion -- an essential element of the kraft chemical recovery process.

The economy of kraft pulping depends on a successful scheme for producing energy and recovering pulping chemicals from black liquor -- a "waste" stream from wood pulping (Hough, 1985). In kraft pulping operations, wood chips are "cooked" in sodium hydroxide and sodium sulfide at elevated temperatures to fragment organic binders and liberate their constituent fibers. The fibers are washed and removed. The resulting wash solution, referred to

as black liquor, contains organic material dissolved from the wood as well as the residual inorganic pulping chemicals. After being concentrated from 15% to approximately 65% solids by weight, the black liquor is burned in a special water-walled furnace, called a recovery boiler. Pressure nozzles spray large drops (1 to 5 mm diameter) into the lower part of the furnace where they dry and burn.

Few references to black liquor drop drying exist in the literature (Monaghan and Siddall, 1963; Bjorkman, 1968; Hulden, 1968; Hupa, 1985). With one exception (Hupa, 1985), the results are mainly qualitative.

Black liquor combustion can be described as occurring in three main stages -- drying, volatiles burning, and char burning. The extent to which these events occur simultaneously, and how they influence each other, is presently not well defined. Behavior is specific to each liquor. However, some generalizations can be made. During drying, drops form a surface skin and repeatedly bubble and burst, often violently. Some volume expansion is observed during this stage. Experimental evidence indicates that drying behavior will influence the final size, shape, and porosity of the dried drop. These, in turn, will affect the rate of combustion through their impact on heat and mass transfer within the particle. For example, Hupa (1985) mentions that the

structure and viscosity of the drying particle will have a significant effect on pyrolysis. The influence of particle swelling during the volatiles burning stage on the char burning rate has been clearly demonstrated (Hupa, 1985). In addition, Moreland and Clay (1985) determined that the maximum reactivity of a black liquor char increased with increasing liquor moisture content, probably due to the influence of moisture evaporation on the physical structure of the char.

The goal of this study is to gain quantitative understanding of kraft black liquor drop drying in air. Of particular interest is the possible influence of surface swelling and rupture on drying rate and drop temperature. Final particle structure is also of interest. A suspended-drop drying apparatus with electronic data acquisition equipment was constructed. Drop drying rates and temperatures were measured in an upflowing stream of heated air. Air temperatures were maintained below the pyrolysis range to insure that mass loss by pyrolysis did not occur.

EXPERIMENTAL EQUIPMENT AND OPERATING PROCEDURES

A drawing of the suspended-drop drying apparatus is shown in Figure 1. A sheathed thermocouple was used to hold a black liquor droplet in place in upflowing heated air. The sheath was bent into a hook and hung from an electronic millibalance.

Surrounding the thermocouple was a Pyrex drying chamber supported by a slide valve. A distinguishing feature of the present system is that a simultaneous record of droplet mass and temperature during drying can be obtained by electronic data acquisition.

Figure 1 here

Major components of the experimental system are described below.

Electronic Millibalance

A Cahn Instruments Inc., Model DTL-3 millibalance was used in weigh-below mode to measure the mass of a suspended drop. The balance is accurate to ± 0.2% over the 0-10 mg range used in this study.

Thermocouple Assembly

The thermocouple assembly was constructed from stainless-steel sheathed thermocouple wire. Thermocouples were individually calibrated prior to use. Recorded temperatures are accurate to ± 2 C over the range covered by the experiments. Both the thermocouple assembly and the drying chamber are shown in Figure 2.

Figure 2 here

Drying Chamber

The double walled drying chamber shielded the thermocouple filament, drying gas, and drop from air drafts in the laboratory. Shown in Figure 2, the chamber is similar in concept to one described by Trommelen and Crosby (1970).

Data Acquisition System

Analog signals from the millibalance and thermocouple were sampled and converted to digital form by an ISAAC (Cyborg Corp.) data acquisition system installed on an Apple II+ microcomputer. Signal averaging was used to reduce random noise.

Drop Formation

Drops were formed with a Hamilton microsyringe having a volume of 10 microliters graduated in 0.1 microliter increments. Squarely honed, 26-gage, hypodermic needles were used. In addition to warming the liquor and syringe, higher solids liquors required shorter needles to minimize pressure drop.

Drying Conditions

Temperatures far below the typical 1000 C temperatures in a recovery furnace were used to prolong drying events, avoid pyrolysis, and facilitate observation. Unless indicated otherwise,

drops were dried under the following conditions, referred to as "standard conditions" in the text:

Initial Drop Volume ..... 2.5 µl

Initial Drop Diameter .... 1.68 mm

Drying Air Temp ..... 167 C

Drying Air Velocity ..... 1.5 m/s.

Black Liquor

The kraft black liquor used in this study was produced by pulping loblolly pine chips under the following conditions:

Sulfidity	25%	Eff. Alkali	16%
Liquor/Wood	4	H-Factor	2000
Cooking Temp.	173 C	Time to Temp.	90 min.
Time at Temp.	94 min.		

Calculation of Drying Rates

Mass versus time data from drying experiments were converted into plots of unaccomplished drying (U.D.) as follows:

U.D. = mass moisture (t)/mass moisture (t=0).

This method of presenting the data minimizes the impact of minor variations in initial droplet mass and any spattering which may have occurred (Trommelen and Crosby, 1970). In most cases, three

runs were averaged to obtain a summary curve of unaccomplished drying versus time.

Curvilinear regression was used to fit a second or third order polynomial to the data (Hayek and Cheetham, 1987). Usually the regression understated the actual curve over the first two or three seconds of drying, but was otherwise a good fit. Typical correlation coefficients exceeded 0.99. Once an accurate fit was obtained, the drying rate was computed by differentiating the polynomial and evaluating it at times of interest.

Calculation of Surface Area

The surface area of black liquor drops was estimated from their videotaped silhouettes. Two steps were involved. First, the perimeter of the silhouette was measured. Next, the diameter of a perimeter-equivalent circle was computed. The surface area of the drop was computed from that diameter.

HEAT TRANSFER MODEL

In simplest terms, ignoring such effects as heats of solution, heat transferred to a moist black liquor drop below the pyrolysis temperature either evaporates moisture (supplies latent heat), or raises the temperature of the drop (supplies sensible heat). If heat inputs are correctly accounted for, measured

drying rates should agree with those estimated from heat transfer considerations.

Heat is transferred to a suspended drop by convection from the flowing gas stream, conduction through the thermocouple wires, and radiation from the surroundings. Equations describing each mode have been developed and verified by Trommelen and Crosby (1970). In our work the same equations were built into an electronic spreadsheet model. The primary purpose of the model was to study the effects of drying behavior -- in particular, drop surface area and temperature -- on drying rate.

A second purpose of the model was to test the assumption that temperature gradients inside the drops may be ignored. Based on that assumption, several researchers have justified using an internal thermocouple to estimate drop surface temperature (Sano and Keey, 1982; Trommelen and Crosby, 1970; and van der Lijn, 1976).

Heat transfer by each mode depends on the temperature driving force and the available area for heat transfer. To estimate drying rate, the model equations require that surface area and drop temperature be described as functions of time. Drying rate is then computed by a simplistic energy balance as:

$$\text{Drying Rate} = \left(\text{Rate of Heat Transfer} - \text{Rate of Sensible Heating}\right) / \text{Heat of Vaporization of Water}.$$

As long as physical data required by the equations are accurate, the extent of agreement between experimental results and model computations will depend on how well the input data describe the true surface area and temperature. Combinations of both assumed and experimental surface area and temperature profiles were input to the model to compute drying rates.

Questions about how well the internal thermocouple estimates the true surface temperature, and whether increased surface area due to inflation results in higher drying rates can be answered by comparing the model results to experimental data. For example, early in drying drops shrink as spheres in proportion to mass loss. During that time, if a discrepancy is found between the model calculations which contain input data for area change proportional to mass loss, it follows that the temperature input does not represent the actual surface temperature.

Three calculation options were considered. Each option and its "what if" question are explained below, where T_S is the drop surface temperature, and S.A. refers to the drop surface area. A likely alternative -- that drop surface temperature differs from that measured by the thermocouple, and that the surface area increases due to inflation -- can be evaluated by comparing the results of these three options below with experimental data.

Option 1 "What if" the drop surface temperature is correctly measured by the thermocouple and the drop surface area shrinks as a sphere proportional to mass loss?

Inputs T_s -- as measured by thermocouple
S.A. -- computed from mass loss data assuming spherical shrinkage

Option 2 "What if" the drop surface temperature is correctly measured by the thermocouple and the drop surface area increases due to inflation?

Inputs T_s -- as measured by thermocouple
S.A. -- experimental surface area data

Option 3 "What if" the drop surface temperature differs from that measured by the thermocouple and the drop surface area shrinks as a sphere proportional to mass loss?

Inputs T_s -- assumed temperature profile
S.A. -- computed from mass loss data assuming spherical shrinkage

WATER DROP DRYING

To verify the heat transfer equations, 2-microliter (diameter = 1.56 mm) water drops were dried in air and the

resulting average drying rate curve was compared to model calculations. In the model, the surface temperature was assumed equal to that of the internal thermocouple. The surface area was assumed to be that of a sphere of water whose mass and temperature equalled those measured experimentally.

Results are plotted in Figure 3. The dashed curve represents the expected drying rate if the effect of mass transfer on heat flux is ignored. The fine solid line includes the correction for mass transfer. A maximum discrepancy of 6 percent exists between the corrected model curve and experiment.

Figure 3 here

Good agreement was due to the fact that the model assumptions for surface area and temperature conform to the drying behavior of water drops. First, water drops tend to shrink as uniform spheres in proportion to mass loss. Second, water drops circulate internally, which minimizes any temperature gradients in the drop. Hence, the thermocouple should measure a temperature which approximates the drop surface temperature.

BLACK LIQUOR DROP DRYING

Unlike pure solvents, which tend to dry uniformly, drops containing dissolved solids exhibit a variety of behaviors when

dried above the boiling point. Charlesworth and Marshall (1960) determined that drops of solutions which form a porous crust show little morphology change during drying. Moisture escapes relatively uninhibited through surface pores and interstices. Drops containing skin-forming solutions which inhibit mass transfer will usually inflate and/or rupture, often repeatedly.

Drop Behavior and Surface Swelling

Kraft black liquor is a skin-forming solution. When dried in air on the suspended-drop drying apparatus, black liquor drops initially shrivel and shrink as moisture evaporates. Surface folding develops in drops whose initial solids concentration is less than 50 percent. With continued heat transfer, the internal temperature increases until the drops suddenly inflate and rupture. Inflation increases the available area for heat transfer. If the drop is still moist, some of the contents may be ejected during rupture. Most often, repeated rupture and inflation continue until the drop is nearly dry. A thin, hollow shell is typically found on completion of drying.

Figure 4 shows the relative surface area histories of nominal 2.5 microliter (diameter = 1.68 mm) black liquor drops drying in air under standard conditions. Before inflating, the drops tend to shrink as spheres. Minor deviations from spherical

shrinkage occur for drops with greater than 20% initial solids, probably due to some internal generation of vapor in the drop shell prior to the burst point. The extent of surface swelling after inflation clearly increases with initial solids.

Figure 4 here

Drop Temperature

Initial liquor solids content has a significant influence on the temperature histories of drying black liquor drops. Shown in Figure 5, initially low solids liquors (30% solids and below) experience a constant temperature period whose length decreases with increasing solids content. The availability of surface moisture in the early stages of low solids liquor drying results in a pseudo wet-bulb temperature (approximately 71 C). Above 40% solids, no constant temperature period exists.

Figure 5 here

A second constant temperature period seems to exist near 120 C in Figure 5. Internal pressure relief from repeated rupture produced depressions in the temperature curves. Swings of 2-5 C were typical. As shown in Figure 6, rupture occurred over the range of solids from 55-65% regardless of initial solids content.

Figure 6 here

Drying Rate

Black liquor drops were dried in air under standard conditions. Experimental and calculated drying rates are compared in Figures 7 and 8 for 30% and 50% solids liquors, respectively. The three combinations of surface area and temperature previously described were used as input to the model equations. A small arrow along the abscissa indicates the average time when bursting first occurred (burst point). Inflation usually preceded bursting by one or two seconds.

Figures 7 and 8 here

As indicated in the legend, the heavy solid curve represents the experimental drying rate. Other curves represent model computations using the three input options for surface area and temperature.

The narrow solid line represents the first option; it assumes that the black liquor drop shrinks as a sphere and that the thermocouple measures the surface temperature. The dashed curve represents the second option. It assumes that the thermocouple measures the surface temperature but uses the experimentally determined surface area rather than assuming spherical shrinkage. Because only minor deviations from spherical shrinkage appear prior to the inflation point, this option is applied only

after inflation has occurred. The dotted curve again assumes a shrinking sphere but uses an assumed linear surface temperature which was found to cause agreement with experimental results. The assumed surface temperature is higher than the drop temperature measured by internal thermocouple (Figure 9). The physical basis for assuming a linear temperature profile relates to the rate of surface skin formation on the suspended drop. More details about the assumed profile and the choice of the beginning and end-point temperatures are given in the discussion section.

Figure 9 here

For 30% solids liquor (Figure 7), comparing the experimental and model curves prior to the burst point indicates that assuming spherical shrinkage and that the thermocouple temperature approximates the true surface temperature causes the model to first overestimate and then underestimate the experimental rate of drying (narrow solid curve). After the burst point, the model parallels the experimental drying rate, understating it slightly.

If observed surface swelling is included, the model predicts more rapid drying after the burst point (dashed curve). However, as shown by the heavy solid curve, increased drying rates due to inflation were not obtained experimentally.

An assumed linear increase from an initial surface temperature of 89.5 C to 121 C at the burst point (Figure 9) with

spherical shrinkage gave excellent agreement with the model until the burst point (dotted curve in Figure 7).

For 50% solids liquor (Figure 8), computations which assume that spherical shrinkage and thermocouple temperatures represent the experimental surface area and temperature, respectively, understate the drying rate along the entire drying curve (narrow solid curve). Nevertheless, the curves parallel each other closely after the burst point.

When the actual inflated surface area is included, the model grossly overpredicts the actual drying rate (dashed curve).

An assumed linear temperature increase from an initial temperature of 110 C to 118 C at the burst point causes agreement between model and experiment until the burst point (dotted curve).

DISCUSSION OF RESULTS

Comparing model calculations and experimental results gives valuable insight into black liquor drying behavior and critical factors which influence drying rate. Drop surface area and temperature are considered separately in the following discussion.

Drop Temperature

For 30% solids black liquor, prior to the burst point, surface area decreases approximately proportional to mass loss

(Figure 10). The deviation of the experimental surface area from spherical shrinkage indicates that some internal voids have formed. When compared to other solids levels (Figure 4), this deviation seems exaggerated, probably due to experimental error. Minor change from spherical shrinkage is more likely. Therefore, deviations from spherical shrinkage are probably not responsible for the discrepancy between experimental and predicted drying rates prior to the burst point. It is more likely that surface temperature and the rate of surface temperature change are responsible.

Figure 10 here

In Figure 7, between 0 and 12 seconds, the model which assumes that the thermocouple accurately measures surface temperature and that the drop shrinks as a sphere proportional to mass loss (thin solid curve) overpredicts the actual drying rate. From 12 to 34 seconds the same model understates the drying rate. Local heat transfer considerations may explain why this occurs.

In an upflowing gas stream, a suspended drop will experience greater convective heat transfer coefficients along its lower face (van der Lijn, 1976). Unless circulation is able to mix the contents of the drop, the underside will tend to dry more quickly. Local hot spots may be created where heat transfer is highest, especially if internal bubbles are able to nucleate there

(El-Sayed, 1987). Since the bottom face is the most distant part of the drop from the thermocouple, the thermocouple will approximate the mean surface temperature only if the Biot number is sufficiently low. As shown in Figure 9, early in drying the thermocouple temperature is less than the assumed surface temperature (the temperature which caused agreement between experiment and model). When the thermocouple temperature is used in the model, an exaggerated estimate of the heat transfer driving force results. Therefore, model computations overpredict the initial drying rate.

The role of sensible heating is also important and cannot be ignored. From 4 to 10 seconds, a pseudo-constant temperature period is observed experimentally. During this time, the slopes of the experimental and assumed temperature profiles are similar. The slope determines the amount of sensible heating computed by the model. As mentioned before, in computing model drying rates, sensible heat is subtracted from the total amount of heat available for drying. Between 4 and 10 seconds, the sensible heating rates are similar for both cases. Therefore, the discrepancy between the experimental and model drying rates is primarily due to the difference in surface temperatures.

After about 12 seconds, the temperature difference in Figure 9 steadily decreases with time. However, the slope of the thermocouple-temperature-versus-time curve increases relative to

the assumed temperature curve. As mentioned, a steeper slope implies more sensible heating and a lower drying rate. Therefore, the estimated curve of drying rate falls below the experimental curve.

One reason for the steeper slope may be that heat conducted through the thermocouple dries the mass near the junction instead of heating the entire drop. Abundant nucleation sites on the thermocouple junction promote the formation of vapor bubbles, increasing the thermal resistance to conduction at the thermocouple site. The temperature sensed by the thermocouple will reflect its dry, "insulated" surroundings and increase rapidly. As shown in Figure 9 after 23 seconds, it may even exceed the surface temperature slightly. The mean temperature driving force estimated by thermocouple would then be less than that for the drop as a whole. After that time, heat transfer predictions assuming that the thermocouple measures the surface temperature would tend to slightly understate the actual rate of heat transfer. It follows that drying rate is also somewhat understated. This effect may be a minor one.

The choice of a linear temperature profile to fit the data prior to the burst point was, at first, arbitrary. However, in a solution capable of creating internal heat transfer

resistance, experimental evidence may justify a linear surface temperature increase.

Charlesworth and Marshall (1960) observed that a vertically symmetrical solid phase forms on the bottom of a suspended, drying drop. The crust advances toward the equator. The rate of advance is initially rapid, but slows as the front approaches the equator.

For any spherical drop, the rate of surface area increase with vertical distance from the bottom of the drop is a constant. This implies that, for a relatively constant drying rate, the vertical rate of surface crust advance will decrease linearly as the crust approaches the equator. If vapor bubbles form in the developing crust (or skin) and produce hot spots, the average rate of surface temperature increase should be linear, also.

Beginning and end-point temperatures for the linear interval were chosen as follows. Bursting was assumed to mix the drop's contents and minimize internal temperature gradients. Therefore, at the burst point the thermocouple temperature was chosen to approximate the surface temperature. The starting temperature was then obtained by iterating until model results and experimental data agreed.

Similar results were obtained with 40% solids liquor. Results for 50% solids liquor were not consistent with those of lower solids. The tendency of these very viscous drops to adhere to the side of the thermocouple rather than completely surround it may be responsible.

Surface Area

Inflation of drops would be expected to increase both heat transfer and drying rates (El-Sayed, 1987). To date, no other researchers have attempted to quantify the effect of inflation on drying rates of drops in air. Experiments indicate that inflation does not cause black liquor drying rates to increase significantly. Because the majority of heat transfer in this system is convective, it seems reasonable to seek an explanation based on convective heat transfer considerations.

Convection heat transfer to the drop is calculated by

$$Q_c = h \bullet A(T_a - T_s).$$

The difference between the ambient air temperature and the drop surface temperature is the external driving force for heat transfer to the drop. The influence of drop inflation on each of these factors is considered below.

Inflation can cause dramatic increases in drop surface area. In the commonly used Ranz-Marshall correlation (Ranz and Marshall, 1952)

$$Nu = hD/k = 2 + 0.6Re^{1/2}Pr^{1/3},$$

h decreases with increasing diameter. The product $h^{\bullet}A$ will increase by virtue of the surface area's higher order dependence on diameter. For example, a typical 50% solids drop whose original diameter is 1.7 mm inflates to a maximum near 2.3 mm during air drying at 167 C, a relative surface area increase of about 1.9 times. The ratio of heat transfer coefficients, $h_o^{\bullet}/h^{\bullet}_{infl}$, is approximately 0.8. At the same time, assuming an equal temperature driving force, the relative convection heat transfer, $(h^{\bullet}A)_o/(h^{\bullet}A)_{infl}$, has increased by a factor of 1.5. A proportional increase in drying rate or sensible heating would be expected.

Since the product $h^{\bullet}A$ increases with inflation, for convection heat transfer to remain relatively constant a proportional decrease in temperature driving force must occur. The air temperature is constant. Therefore, it follows that the surface temperature must increase as a result of inflation. Apparently, the increase is not sensed by the internal thermocouple. A probable explanation is that evaporation creates an internal resistance to heat conduction within the drop.

The possibility that vapor bubbles forming inside a drying drop could contribute to local hot spots was mentioned by El-Sayed (1987). A hot spot will result if vapor bubbles nucleate just below the surface and increase local resistance to heat conduction. If adequate conduction paths around a vapor bubble exist, the influence of one or several hot spots on overall heat transfer might not be significant. On the other hand, if multiple small vapor bubbles could form, they would act as a porous insulator. As a consequence, few, if any, good conduction paths would exist within the drop. The surface temperature would rise with increasing vapor bubble volume fraction in the moist drop wall.

Nucleation and growth of multiple vapor bubbles are promoted by low diffusivity and high viscosity (El-Sayed, 1987). Both would be expected in kraft black liquor, especially at solids levels in excess of 50% (Hough, 1985).

Scanning electron microscopy confirmed that multiple small vapor bubbles can form in a black liquor drop drying under standard conditions. Figure 11 shows the cross section of a previously dried, 22% solids black liquor drop magnified 300 times. Two large vapor pockets are evident in the drop wall. Striations on the inner surface of the drop (lower left hand portion of the image) may be the result of vaporization occuring along stress lines caused by inflation and bursting.

Figure 11 here

Further magnification of the upper left-hand corner of the smaller vapor pocket indicates the presence of small vapor bubbles (Figure 12) . Coalescence of many small bubbles appears to be responsible for the presence of larger pockets.

Figure 12 here

Mechanism of Surface Temperature Rise

A mechanism for surface temperature rise during black liquor drop drying is implied from the results above. First, a skin forms on drops exposed to upflowing hot air. The skin eventually covers the drop. Any circulation ceases with the completion of the surface crust. Concentration gradients in the outer shell become steeper as drying continues.

Desorption of air and the presence of inorganic precipitates promote nucleation of vapor bubbles in the moist drop (Greenwald and King, 1982). Once formed, bubbles tend to grow due to further vaporization of water from bordering liquid. Additional drying increases the resistance to moisture movement. As diffusion becomes limiting, multiple small bubbles form in preference to larger single bubbles (El-Sayed, 1987). Even prior to inflation, surface temperature rises as internal thermal resistance grows.

Small bubbles may combine to form larger pockets until high viscosity and low diffusivity prohibit coalescence. Large pockets will eventually burst or become immobilized in the drop shell as it dries (Figs. 11 and 12). If vaporization rates are sufficient, the drop will inflate, increasing the area for heat transfer. Rapid heating results, which quickly dries the outer shell of the drop. The surface temperature increases in response to inflation and the inhibited conduction path to the moist interior.

Bursting will occur when internal pressure from evaporating moisture exceeds the surface strength. For suspended drops under standard conditions, this occurs near 60% solids and 120 C (Figure 6). When deflated, temperature gradients will diminish as conduction within the drop improves. However, this will tend to increase the external temperature driving force, enhance heat transfer, and lead to another round of inflation and bursting.

The overall result of the cycle of inflation (with proportional surface temperature increase) and deflation (with proportional surface temperature decrease) is relatively constant drying rate. No dramatic increase in drying rate due to inflation results.

IMPLICATIONS

Black liquor drops exposed to high temperatures in a typical recovery boiler inflate and burst violently. In contrast to low temperature drying in which the drops tend to vent through one location, at furnace temperatures bursting occurs over the entire surface. Rather than forming a hollow shell typical of low temperature drying, a more homogeneous, porous particle may result. If mixing is able to reduce the temperature and concentration gradients within the particle, it should dry at sufficiently low temperatures to avoid significant surface pyrolysis until the entire particle is dry. On the other hand, if internal voids increase the conduction heat transfer resistance in a way similar to that for low temperature air, even when the majority of the drop is still moist high particle surface temperatures should cause significant simultaneous pyrolysis. In addition, if bursting is forceful enough to expel "fingers" of liquor, these could dry and pyrolyze before surface forces are able to gather them back into the drop. High temperature drying is currently the focus of continuing research.

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NOTATION

A = drop surface area, m^2

C_p = average heat capacity of drying medium, J/(kg)(K)

D = average drop diameter, m

h = average heat transfer coefficient between drop and drying medium, W/m^2K

$h^\bullet$ = average heat transfer coefficient between drop and drying medium corrected for mass transfer, W/m^2K

k = average thermal conductivity of drying medium, W/mK

Nu = Nusselt number, hD/k, dimensionless

Pr = Prandtl number, $C_p\mu/k$, dimensionless

Q_c = rate of convection heat transfer to drops, W/s

Re = drop Reynolds number, DV/ν, dimensionless

T_a = temperature of drying air, K

T_s = temperature of drop surface, K

V = average linear velocity of drying air, m/s

ν = average kinematic viscosity of drying air, m^2/s

μ = average viscosity of drying air, kg/(m)(s)

Subscripts

o = initial value (at t=0)

infl = value for inflated drop

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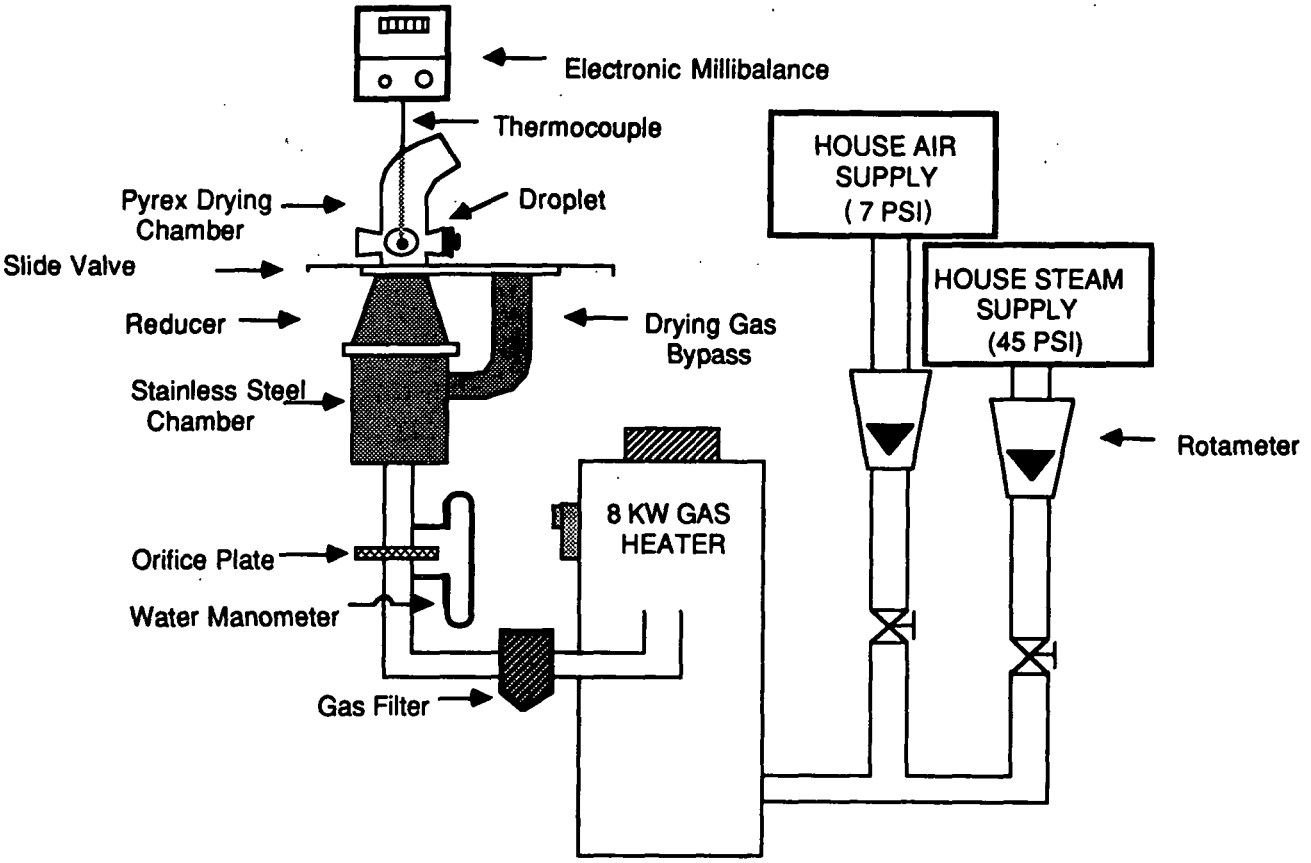

Figure 1. Experimental apparatus used to dry suspended black liquor drops in heated air. Drop temperature and mass during drying were recorded by electronic data acquisition equipment (not shown).

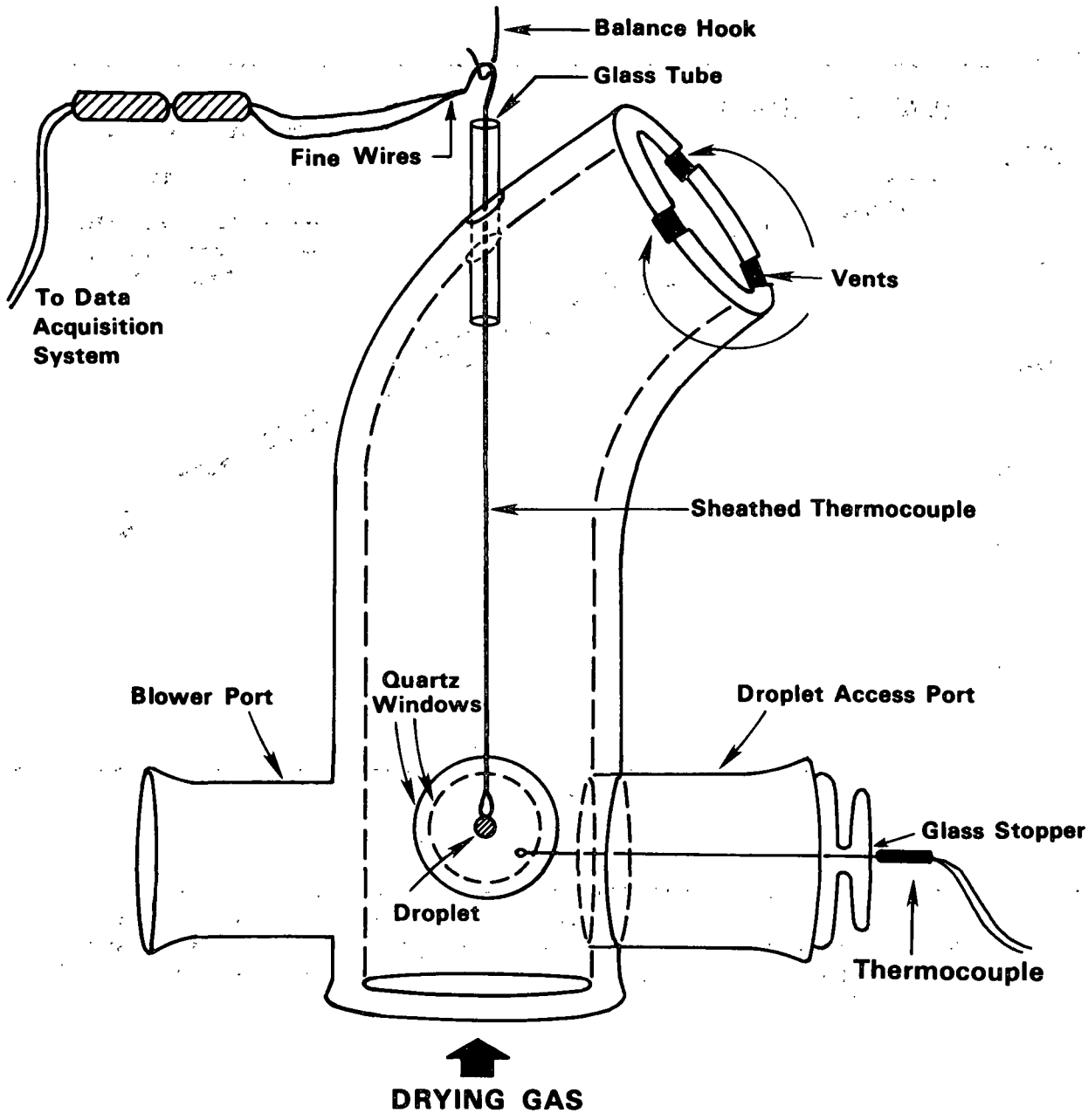

Figure 2. Glass drying chamber and thermocouple assembly.

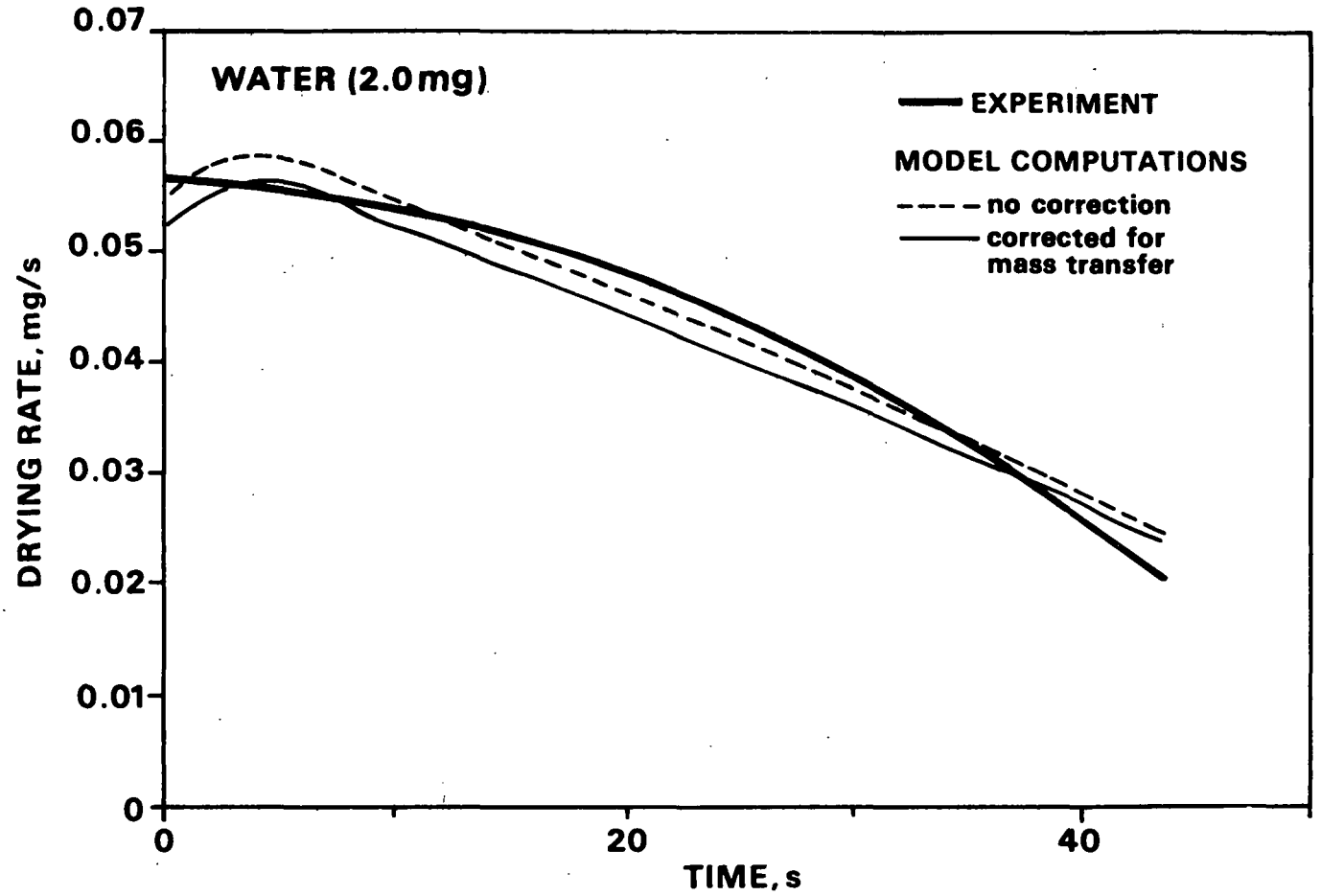

Figure 3. Comparison of water drop drying rate with heat transfer model. In this case, the model assumes that drop surface area shrinks as a sphere in proportion to mass loss by evaporation. It also assumes that the thermocouple measures the surface temperature. [T_a = 167 C, V = 1.5 m/s].

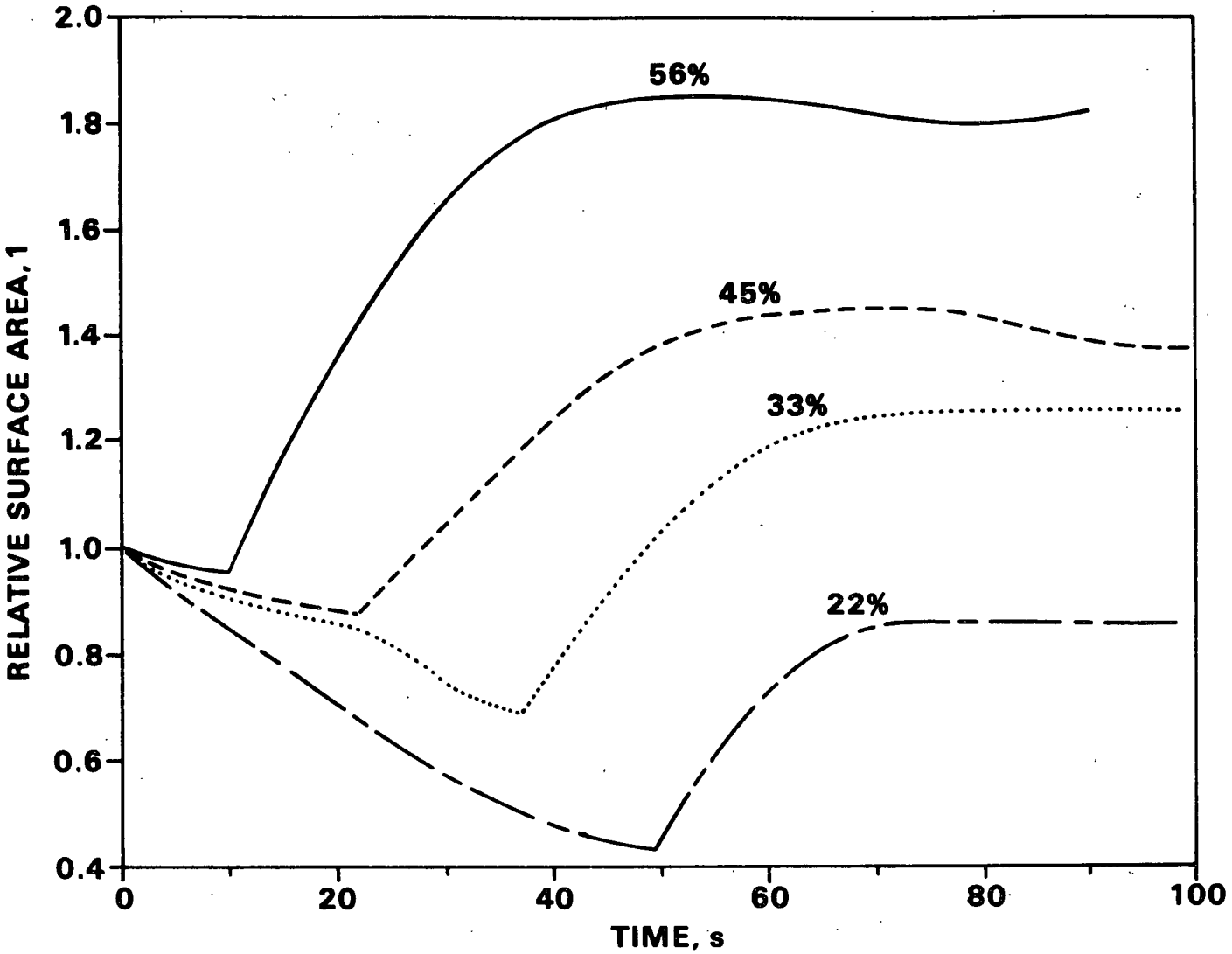

Figure 4. Average relative surface area change of black liquor drops drying in air. [D_o = 1.68 mm, T_a = 167 C, V = 1.5 m/s].

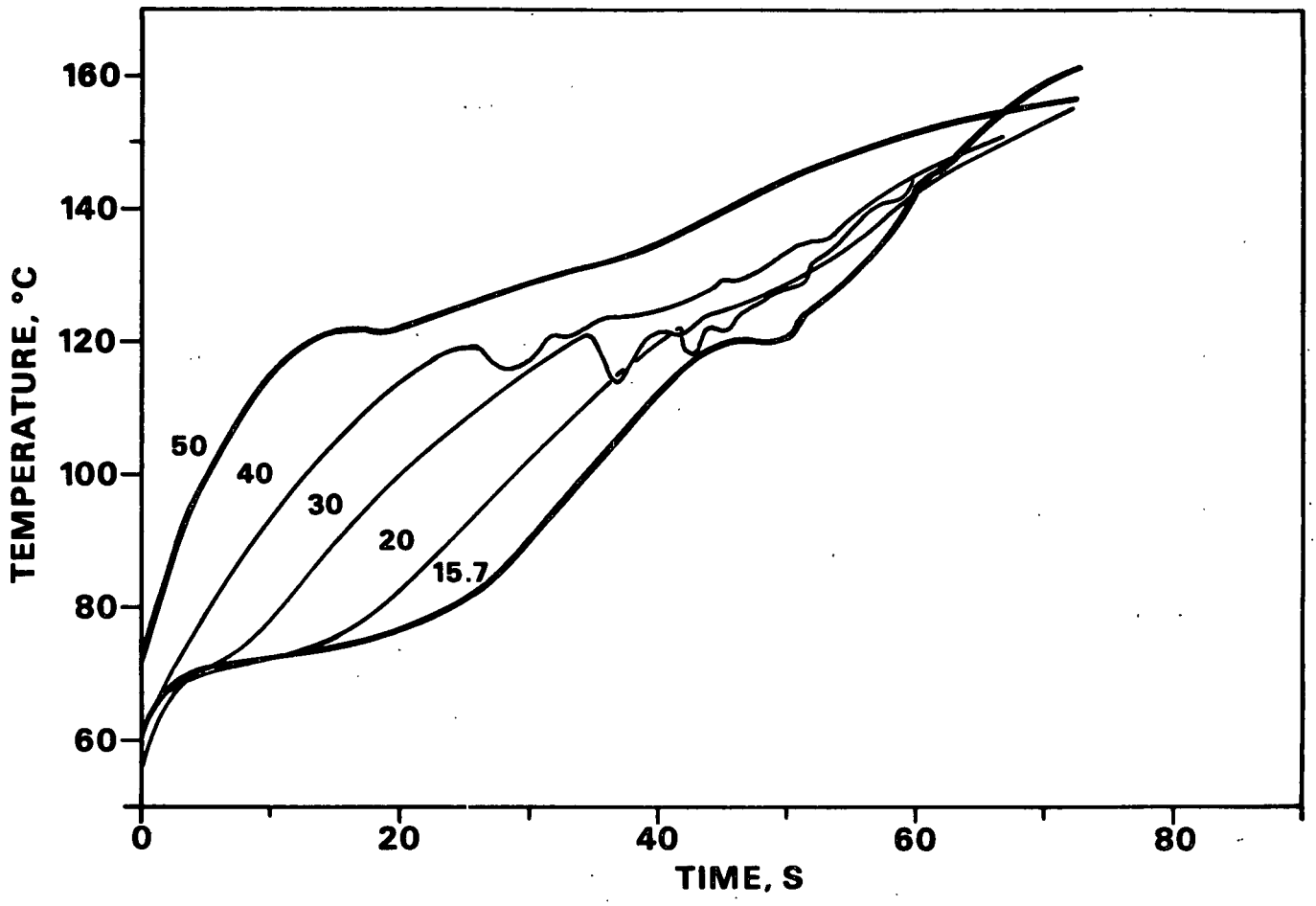

Figure 5. Temperature history of black-liquor drops drying in air as recorded by internal thermocouple. Parameter is initial solids content. Bursting of drops is responsible for depressions near 120 C. [D_o = 1.68 mm, T_a = 167 C, V = 1.5 m/s].

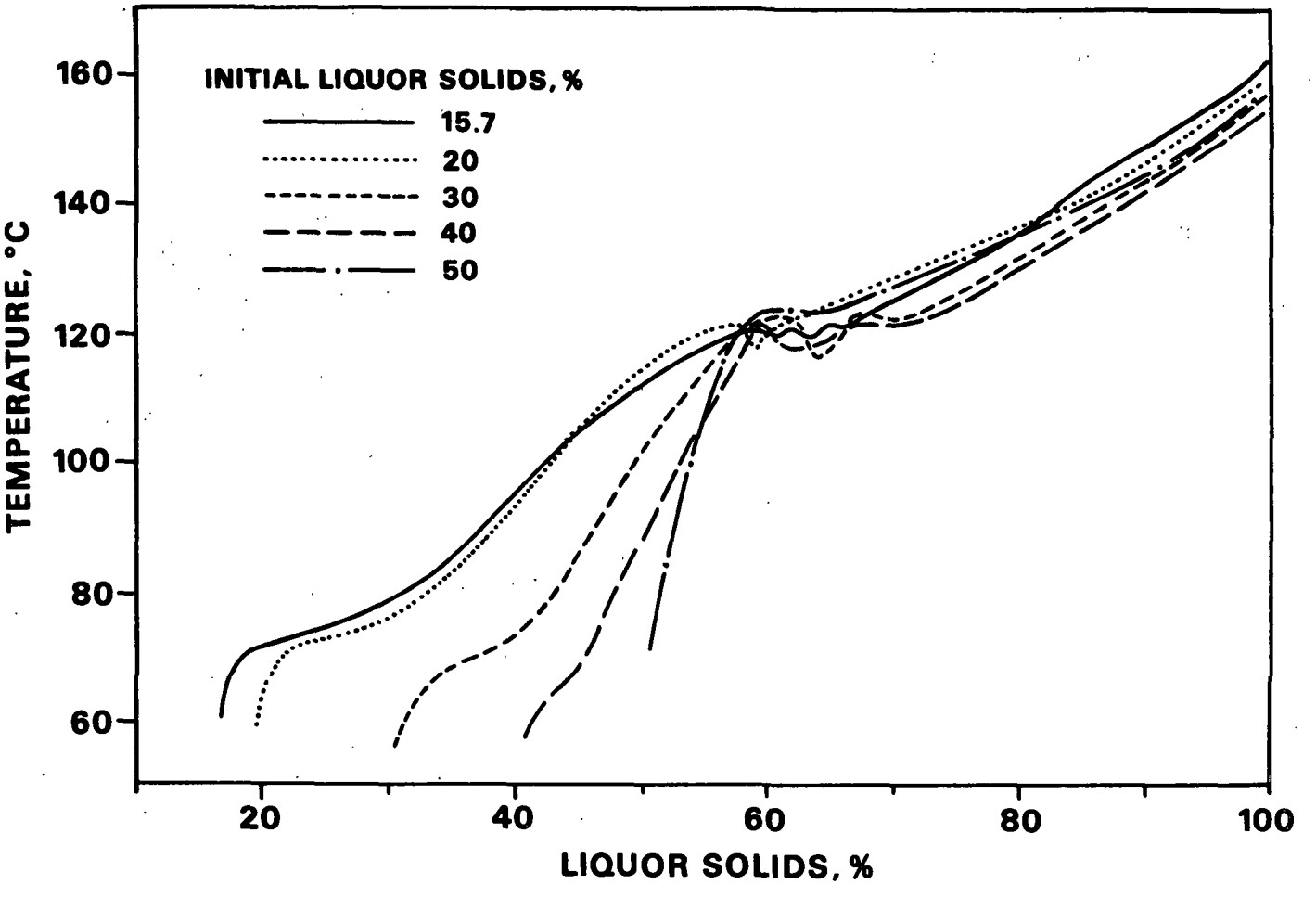

Figure 6. Temperature vs. solids history of black liquor drops drying in air as recorded by internal thermocouple. Bursting occurred near 60% solids, 120 C in all cases. [D_o = 1.68 mm, T_a = 167 C, V = 1.5 m/s].

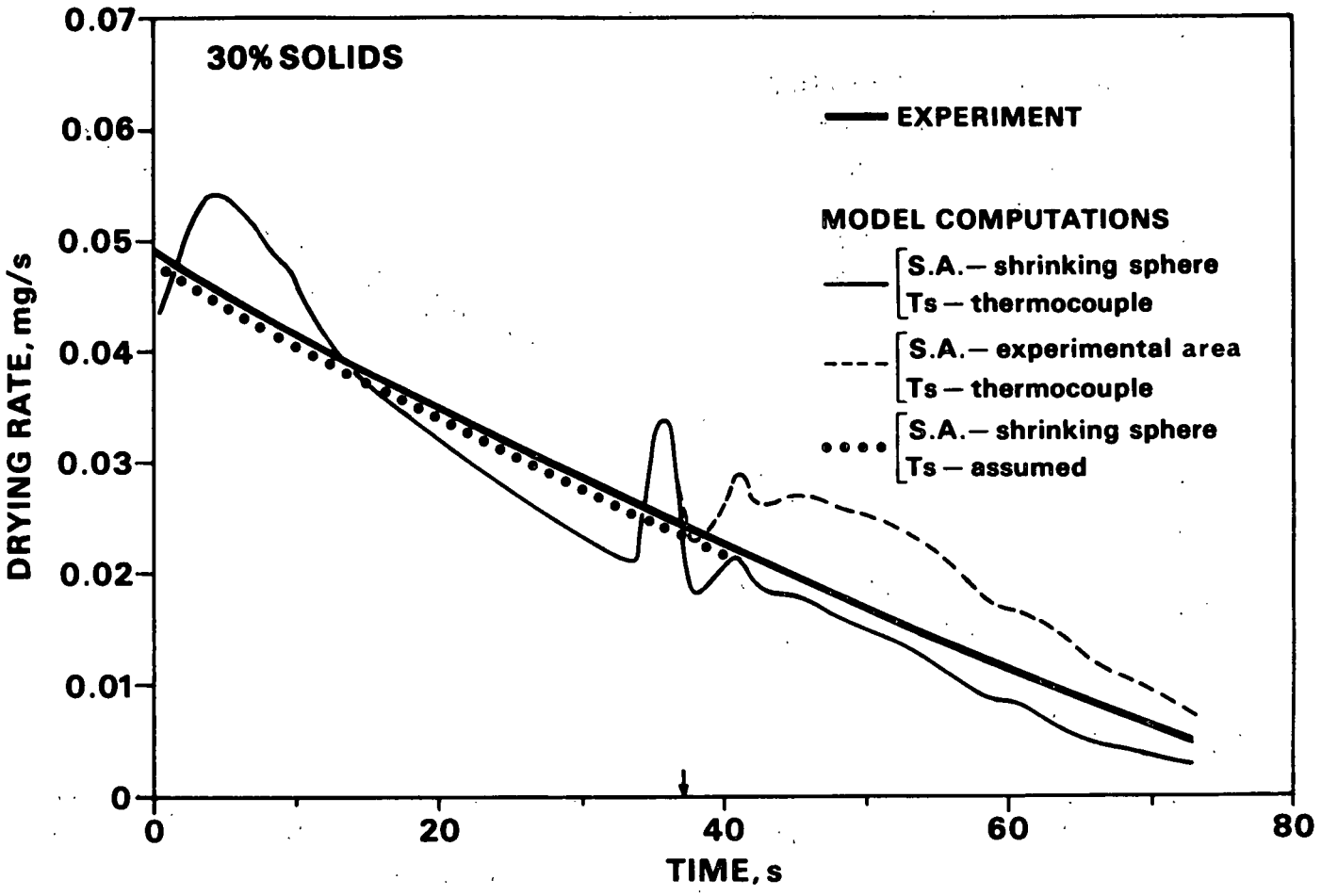

Figure 7. Experimental vs. Model Results for 30% Solids Black Liquor Dried in Air.

Comparison of black liquor drop drying rate with heat transfer model results for three surface area (S.A.) and surface temperature (T_s) input options. Initial liquor solids is 30%. The thin, solid curve results from assuming that the drop surface area decreases as a sphere in proportion to mass loss, and that the internal thermocouple measures the surface temperature. The dashed curve after the burst point (indicated by small arrow along the abscissa) results from including the experimental surface area, and assuming that the thermocouple measures the surface temperature. The dotted curve is obtained by assuming that the surface area decreases as a sphere in proportion to mass loss, and that the surface temperature increases linearly from 89.5 to 121 C at the burst point. The basis for a linear surface temperature rise is explained in the text. [Initial mass = 3.2 mg, T_a = 167 C, V = 1.5 m/s].

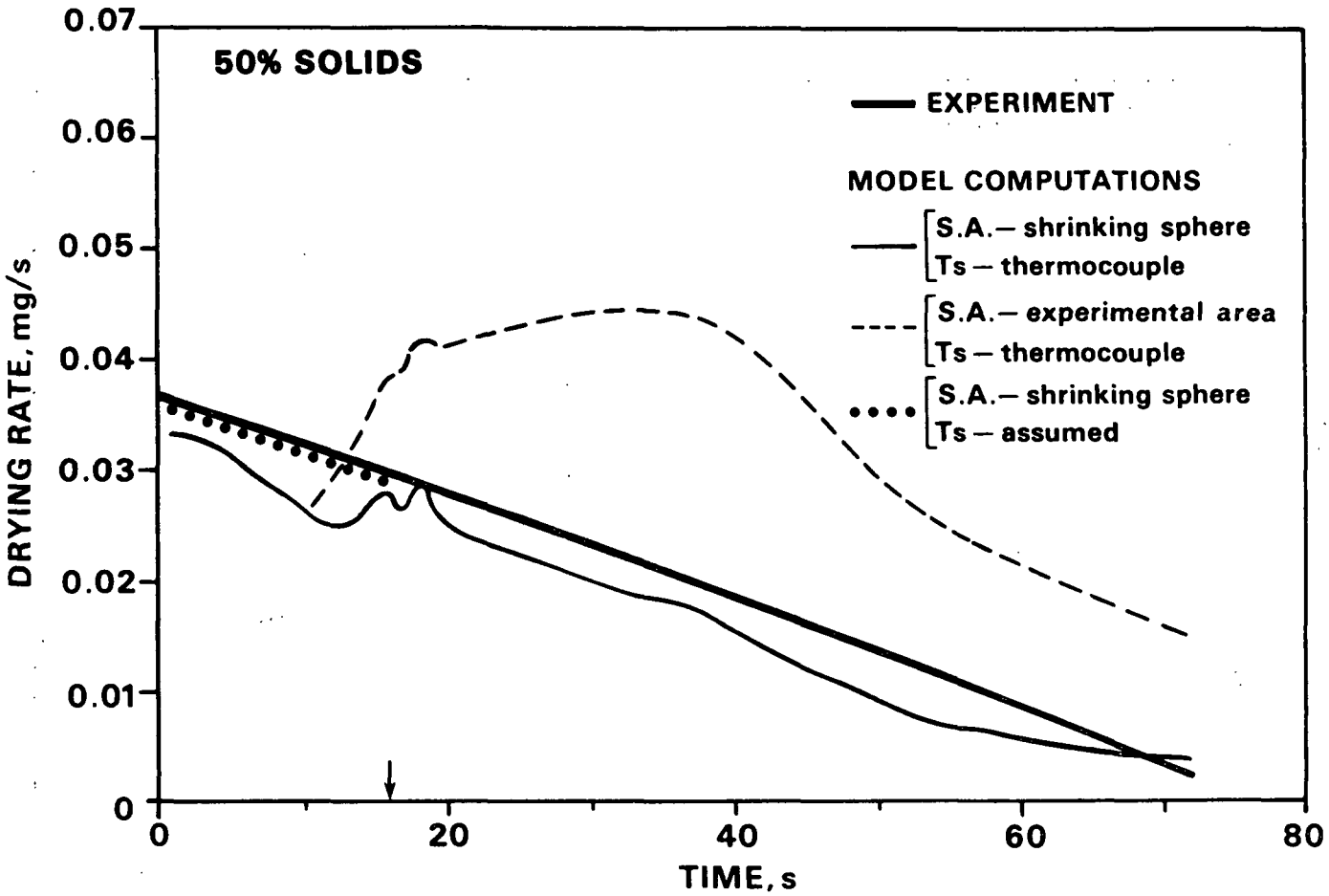

Figure 8. Experimental vs. Model Results for 50% Solids Black Liquor Dried in Air.

Comparison of black liquor drop drying rate with heat transfer model results for three surface area (S.A.) and surface temperature (T_s) input options. Initial liquor solids is 50%. The thin, solid curve results from assuming that the drop surface area decreases as a sphere in proportion to mass loss, and that the internal thermocouple measures the surface temperature. The dashed curve after the burst point (indicated by small arrow along the abscissa) results from including the experimental surface area, and assuming that the thermocouple measures the surface temperature. The dotted curve is obtained by assuming that the surface area decreases as a sphere in proportion to mass loss, and that the surface temperature increases linearly from 110 to 118 C at the burst point. The basis for a linear surface temperature rise is explained in the text. [Initial mass = 3.0 mg, T_a = 167 C, V = 1.5 m/s].

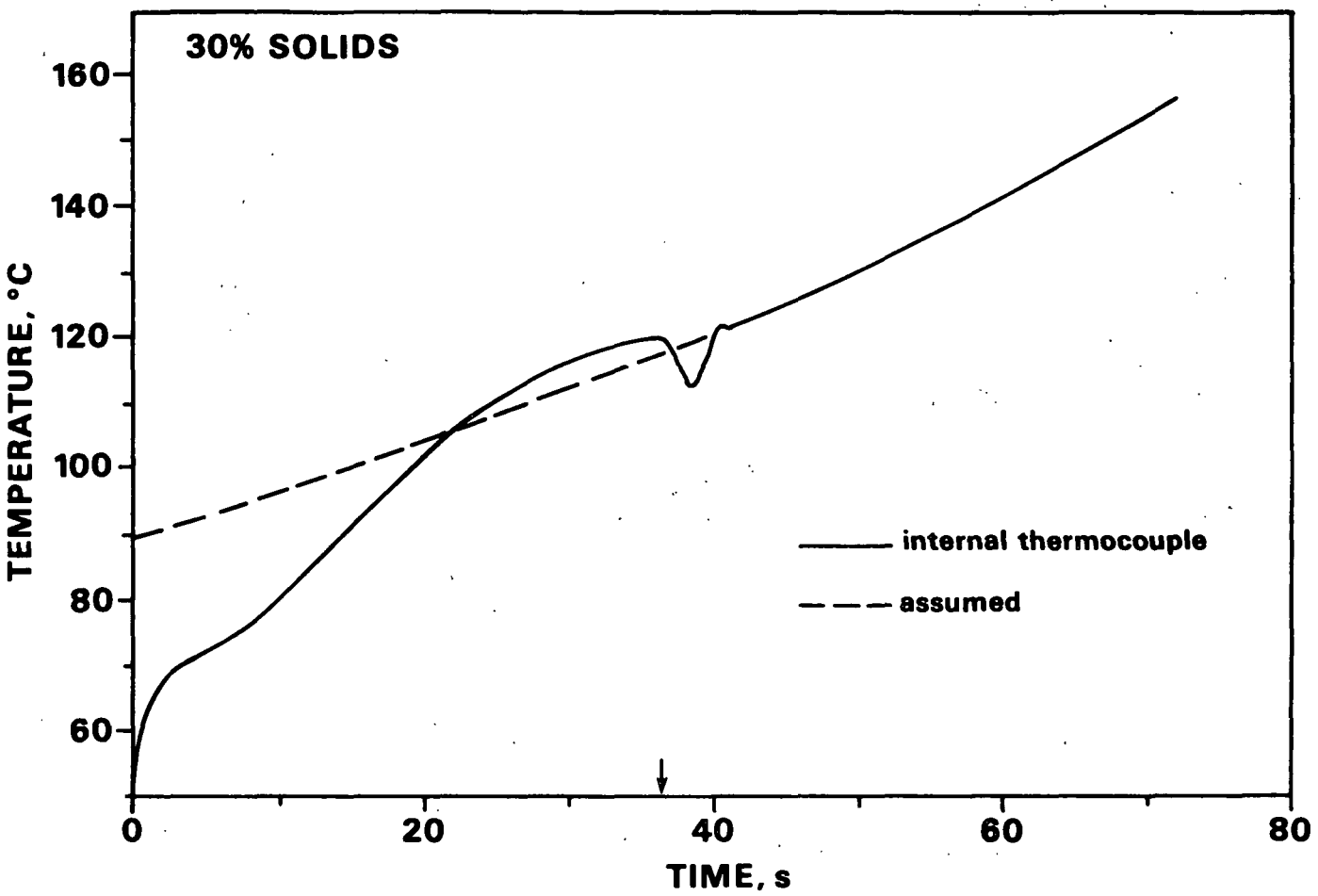

Figure 9. Comparison of drop temperature by thermocouple with assumed linear temperature profile (which caused agreement between model and experiment). [Initial liquor solids: 30%, T_a = 167 C, V = 1.5 m/s].

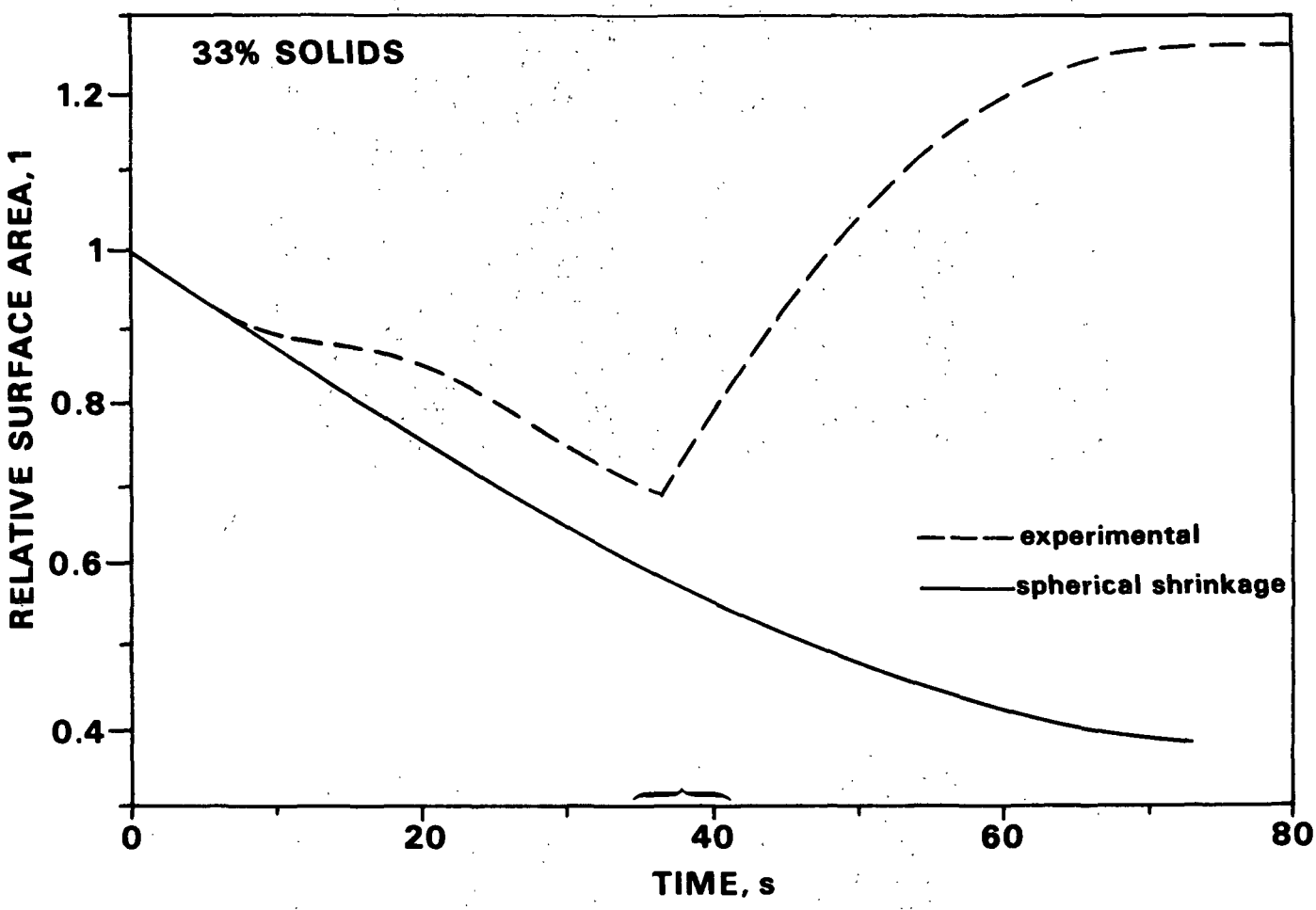

Figure 10. Average relative surface area change of a 33% initial solids drop drying in air. The solid curve illustrates spherical shrinkage proportional to mass loss. The dashed curve represents the surface area of inflated drops from video images. Bracket indicates range of times during which bursting occurred. [D_o = 1.68 mm, T_a = 167 C, V = 1.5 m/s].

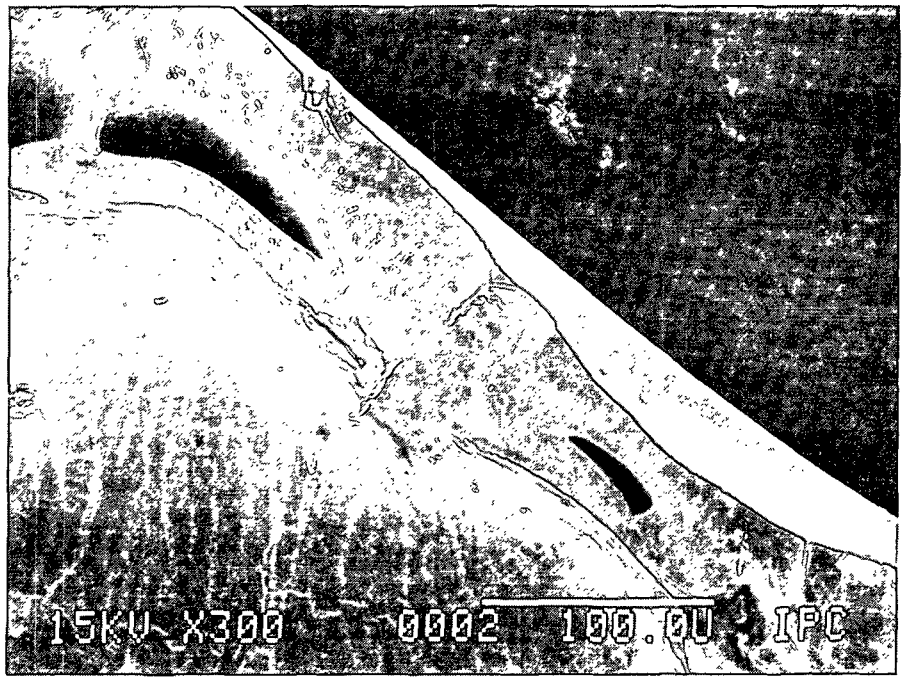

Figure 11. Scanning electron micrograph of the cross section of a hollow black liquor drop. Two vapor pockets are visible in the drop wall which runs diagonally in the figure. Initial solids was 22%. [D_o = 1.68 mm, T_a = 165 C, V = 1.5 m/s].

Figure 12. Enlarged view of the upper left hand corner of the smaller vapor pocket from Figure 11 showing what appear to be small bubbles surrounding the larger pocket. Coalescence of many small bubbles may be responsible for the growth of larger vapor pockets.